Phase chemistry and comparative geochemical behaviour of glassy residues from high temperature solid waste treatment

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Any form of waste treatment produces some residue enriched in unwanted and/or inseparable compounds, heavy metals in particular. Examples are fly ash and residues from flue gas cleaning of municipal solid waste incineration that are enriched in heavy metals, including Pb, Zn, Cu, Cd, as well as dioxins and furanes. Viable strategies for such residues include thermal treatment at high temperature to produce relatively inert glass and possibly a metallic fraction, and, for cost-effectiveness, underground burial in existing caverns from mining activities.

This study provides a detailed account of the phase chemistry and element distribution in glassy products from several high-temperature industrial or laboratory-scale processes. The long-term leaching behaviour is addressed in this context and discussed in the light of current regulatory practice.

Sample material and analytical methods

Products from three different processes were examined: 1) AshArc Process (ABB, laboratory scale) for fly ash and/or bottom ash employing a DC-arc furnace with graphite electrode at 1500°C, including separation of a molten metal alloy, 2) DEGLOR process (ABB, industrial scale) for fly ash using a furnace with molybdenum bath electrodes at 1400°C, and 3) HSR process (Von Roll—Holderbank, laboratory scale) for treatment of residues of municipal solid waste incineration using a smelting furnace with graphite electrodes at about 1500°C.

Analytical methods include reflected and transmitted light microscopy on doubly polished thin sections, X-ray diffractometry, scanning electron microscopy coupled with energy-dispersive chemical analysis (EDS), and electron microprobe analysis (EMP) using wavelength-dispersive spectrometers. Bulk chemistry was determined by X-ray fluorescent analysis. Pb and Cd were determined by Atomic Absorption Spectroscopy following acid digestion.

Phase chemistry and element distribution

All samples are entirely vitreous by macroscopic examination but invariably include a variety of microscopic, predominantly metallic inclusions and/or silicate or oxide crystallites.

AshArc product: Samples consist of very few larger (100 μm) complex Fe-S inclusions and numerous very small (< 3 μm) Fe-S, or abundant two-phase inclusions (< 30 μm) of an Fe-core and an Fe-S-rim. The inclusions are enriched in Cu, Pb and most likely also in Sb and Cd. Pb occurs frequently in minute metallic or sulphidic specks associated with the Fe-rich inclusions. The aerial proportion of metallic inclusions is less than 1 %. Minute crystallites of inferred chromian spinel (Cr-Zn EDS signal) may also occur and some probable feathery-textured Ca-pyroxene. The glass matrix is chemically homogenous. The bulk composition is summarized in Table 1.

DEGLOR product: Some samples display flow banding resulting from light scattering on minute metallic inclusions. Inclusions are frequent and smaller than 1.5 μm but amount to less than 0.15 % by area. The inclusions consist of an Fe-Zn-S phase with frequent minute specks of a Pb-rich phase. The glass matrix is chemically homogenous. The bulk composition is summarized in Table 1.

HSR product: The glassy material displays flow banding resulting from uneven Cr-distribution. Few metallic inclusions could be detected, consisting of a iron core and a copper-iron-sulphide rim. In the glass matrix some chromian spinel inclusions can be observed: EMP analyses reveal Cr_2O_3 contents of 55 wt.% and higher Zn concentrations than the glassy matrix. The bulk composition is summarized in Table 1.

Modelling approach of leaching behaviour

The modelling approach consists of a coupled reactive transport or reaction-path model, and in

TABLE 1. Major and trace element bulk composition of glassy products. (n.d.= not detected)

wt.%	AshArc	DEGLOR	HSR
SiO_2	44.0	44.3	45.4
Al_2O_3	16.9	12.1	15.5
TiO_2	2.2	0.7	1.5
FeO	6.5	1.3	6.9
MgO	3.1	2.1	3.5
MnO	0.3	0.1	0.1
CaO	18.6	32.2	17.9
Na_2O	3.1	3.2	4.8
K_2O	1.9	0.9	0.9
P_2O_5	0.9	0.5	0.3
ppm			
Cu	470	32	694
Zn	610	2550	447
Cr	930	1460	3668
Ba	1830	440	2275
Pb	50	92	34
Cd	0.015	0.25	n. d.

parallel, long-term flow-through column experiments. Column experiments are currently running under moderate acidic conditions (pH 4.0) with monitoring of effluent chemistry.

For the numerical model a component-specific approach is chosen using specific reaction rates and tabulated or estimated equilibrium constants for phase dissolution / precipitation and aqueous complexation. Such models are general and flexible with respect to the chemical environment but require some characterized initial and boundary conditions, and detailed knowledge of the phase chemistry. It is expected, analogue to the modelling of cement degradation, to describe satisfactorily the main phase reaction which determine the Eh-pH conditions of the solution. Special attention has then be held on the release of trace metals.

Discussion

A detailed understanding of the phase chemistry and mineralogy of products from thermal waste treatment allow for an improved understanding of both, the thermal process itself, and the long-term behaviour of the material either under conditions of integration as a secondary raw material (e.g. in concrete or ceramic building materials), or under conditions of a repository. Current regulatory practice in Switzerland takes little advantage of more detailed characterization of residues to originate possible harmful species to explain e.g. contrasting leaching behaviour of soluble (salts, sulphides) *vs* inert compounds (Zn in glass, silicate, oxide; Cr in spinel). Currently only short-term leaching tests under moderate acidic conditions are defined, which simulate 100 years acid rain deposition.

Residues are often compared in terms of bulk composition to average crustal rocks, although without a detailed mineralogical account and its implications, or without consideration of naturally occurring variations. We propose that the issue should be addressed in a more petrologic and geochemical context. Some regulatory efforts (e.g. Dutch Material Building Code) do take a more integral approach, but the current trend dominated by cost-effectiveness provides little incentive for optimized and available technologies for avoidance, separation, re-use and waste treatment.